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(54) **Process for the production of carboxylic acid anhydrides.**

(57) The solubility and stability of rhodium catalysts in rhodium-catalysed carbonylation of alkyl esters or alkyl ethers under substantially anhydrous conditions to produce carboxylic acid anhydrides is improved by the use of co-promoters selected from the group:
1,3-dialkyl-4-methylimidazolium iodide;
1,3-dialkyl-4-ethylimidazolium iodide;
1,3-dialkyl-4-n-propylimidazolium iodide;
1,3-dialkyl-4-isopropylimidazolium iodide;
1,3-dialkyl-4-n-butylimidazolium iodide
1,3-dialkyl-4-sec-butylimidazolium iodide
1,3-dialkyl-4-tert-butylimidazolium iodide;
1,3-dialkyl-2,4,5-trimethylimidazolium iodide and mixtures thereof where the alkyl groups are independently C₁ to C₂₀ alkyl.

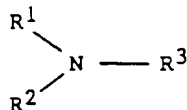
EP 0 479 463 A2

This invention relates to a carbonylation process and in particular to a rhodium-catalysed liquid phase carbonylation process for the production of carboxylic acid anhydrides.

Carbonylation processes are known in which small organic molecules such as alkenes, alkynes, alcohols, esters or ethers are reacted with carbon monoxide in the liquid phase and in the presence of a transition metal catalyst, for example rhodium. When esters or ethers are used as reactants carboxylic acid anhydrides can be produced. It is usual in such processes to use a halide promoter for the transition metal catalyst and often also a further co-promoter to stabilise the catalyst.

Thus, UK patent 1538783 describes a process for the preparation of an anhydride of a monocarboxylic acid which comprises reacting carbon monoxide, an iodide or bromide and a carboxylic ester and/or a hydrocarbyl ether, under substantially anhydrous conditions in the presence of a Group VIII noble metal catalyst and in the presence of a multiple promoter comprising at least one metal of Groups IVB, VB and VIB or a non-noble metal of Group VIII and an organo-nitrogen compound or an organo-phosphorus compound wherein the nitrogen and the phosphorus are trivalent.

According to GB 1538783 the organo-nitrogen co-promoter is preferably an amine, especially a tertiary amine of the formula:



where R^1 , R^2 and R^3 are the same or different and are alkyl, cycloalkyl, aryl or acyl groups which may be substituted by non-interfering groups preferably having up to 20 carbon atoms such as trimethylamine, triethylamine, triphenylamine or ethylenediamine tetraacetic acid or a heterocyclic amine or an imidazole, such as imidazole or methyl imidazole or an imide of a carboxylic acid or a nitrile or amide or an oxime. The promoters are said to stabilize the catalyst and inhibit corrosion.

US patent 4,430,273 describes a process for making acetic anhydride by reacting at least one substance selected from methyl acetate and dimethylether with carbon monoxide under substantially anhydrous conditions, at temperatures of 350 to 575K and under pressures of 1 to 300 bars in the presence of a catalyst system comprised of noble metals belonging to group VIII of the periodic system of the elements or their compounds and at least one substance selected from iodine and its compounds, which comprises using a promoter system consisting essentially of an aliphatic carboxylic acid with 1 to 8 carbon atoms and at least one heterocyclic aromatic compound, in which at least one hetero atom is a quaternary nitrogen atom.

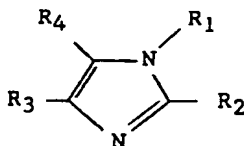
According to US 4,430,273 suitable promoters comprise:

(a) N-methylpyridinium iodide; N,N-dimethylimidazolium iodide; N-methyl-3-picolinium iodide; N-methyl-2,4-lutidinium iodide; N-methyl-3,4-lutidinium iodide; N-methyl-quinolinium iodide;

(b) pyridinium acetate; N-methylimidazolium acetate; 3-picolinium acetate; 2,4-lutidinium acetate; 3,4-lutidinium acetate.

Our published European patent application, EP 0153834 teaches the use of a thiol or an imidazole to stabilise the rhodium catalyst system and prevent loss by precipitation in a process for the liquid phase carbonylation of an alcohol, ester or ether by reaction with carbon monoxide in the presence of rhodium catalyst system comprising a rhodium component and an iodide or bromide component.

The imidazole is said to have the general formula:



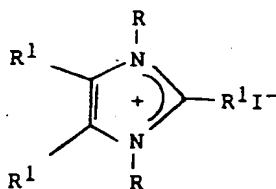
in which R_1 , R_2 , R_3 and R_4 are each independently hydrogen, alkyl, aryl, cycloalkyl or alkaryl hydrocarbyl radicals. A preferred imidazole is said to be N-methylimidazole and this is the only imidazole illustrated by experimental example.

With the use of such co-promoters there is sometimes a tendency for precipitation and/or instability of

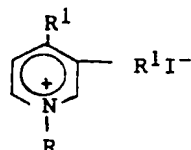
the rhodium catalyst especially under unfavourable process conditions.

Our European patent application publication number EP 0391680A1 published after the priority date of the present application describes the use of certain selected quaternary ammonium iodides as catalyst stabilisers for rhodium catalysed carbonylation of an alcohol or its ester to a carboxylic acid in the presence of water. The catalyst stabilisers are selected from the group consisting of quaternary ammonium iodides having the formula:

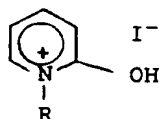
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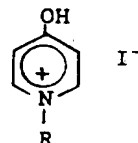
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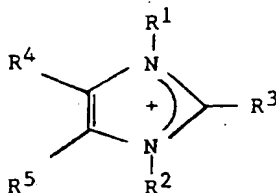
or



wherein the R and R¹ groups are independently selected from hydrogen or C₁ to C₂₀ alkyl groups with the proviso that at least one R¹ group is other than hydrogen.

According to EP 0391680A1 it is preferred that at least one of the R groups is the same as the R² group comprising the organic moiety of the alcohol, iodide derivative and carboxylic acid. The R¹ groups on the other hand are suitably hydrogen or C₁ to C₈ alkyl, preferably hydrogen or C₁ to C₆ alkyl with the proviso defined above. Examples of preferred catalyst stabilisers in each of classes (1) and (2) are said to be those where the R¹ groups are selected from hydrogen, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl and t-butyl.

One particularly preferred class of catalyst stabilisers is said to be iodide salts of the cation:-



Where

(i) R¹ and R² are methyl

(ii) R⁵ is hydrogen

(iii) R³ is C₁ to C₂₀ alkyl or hydrogen

and

(iv) R⁴ is C₁ to C₂₀ alkyl.

Most preferred examples of this class are said to be where (1) R³ = C₂H₅, R¹, R² and R⁴ = CH₃ and R⁵ = H or (2) R³ and R⁵ = H, and R¹, R² and R⁴ = CH₃.

The carbonylation process of EP 0391680 A1 differs from that of the present invention in that it produces carboxylic acids from alcohols or their esters in the presence of a finite amount of water in the reactor. The process of the present invention on the other hand produces carboxylic acid anhydrides from

esters and/or ethers substantially in the absence of water in the reactor.

The technical problem to be solved by the present invention is to provide a co-promoter for rhodium-catalysed liquid phase carbonylation processes for the production of carboxylic acid anhydrides under substantially anhydrous conditions which reduces the tendency for precipitation and/or instability of the rhodium catalyst.

Thus according to the present invention there is provided a process for the production of a carboxylic acid anhydride comprising reacting in a reaction zone under substantially anhydrous conditions, carbon monoxide with a carboxylic acid ester or an alkyl ether in the presence of a rhodium catalyst, an iodide promoter and a co-promoter characterised in that the co-promoter is selected from the group consisting of

1,3-dialkyl-4-methylimidazolium iodide;
1,3-dialkyl-4-ethylimidazolium iodide;
1,3-dialkyl-4-n-butylimidazolium iodide;
1,3-dialkyl-4-sec-butylimidazolium iodide; 1,3-dialkyl-4-tert-butyl imidazolium iodide; 1,3-dialkyl-4-n-propylimidazolium iodide;
1,3-dialkyl-4-isopropylimidazolium iodide;
1,3-dialkyl-2,4,5-trimethylimidazolium iodide and mixtures thereof where the alkyl groups are independently C₁ to C₂₀ alkyl, preferably methyl or ethyl, more preferably methyl.

The present invention solves the problem defined above by using certain selected quaternary ammonium iodides which have been shown not to generate sparingly soluble rhodium containing complexes even under severe conditions which have been designed to exacerbate rhodium catalyst instability.

By substantially anhydrous conditions in the reaction zone is meant a complete absence of water or a water concentration of less than 0.1% by weight.

The process of the present invention may be operated as a batch or a continuous process, preferably a continuous process. When operated as a continuous process, reaction medium may be continuously removed from the reaction zone and the carboxylic acid anhydride separated therefrom prior to recycle of the catalyst and promoters to the reaction zone. It is during such separation of catalyst and promoters from the reaction medium for example, that rhodium catalyst precipitation can occur due to, for example, a deficiency of carbon monoxide relative to the reaction zone. It is believed that the co-promoter of the present invention can provide improved solubility and stability of the rhodium catalyst in such separations and hence allow for increased productivity and/or reaction at more moderate conditions.

The carboxylic acid ester and alkyl ether preferably have 2 to 6 carbon atoms. Preferred reactants are methyl acetate, ethyl acetate and dimethyl ether. A controlled amount of alkanol, for example methanol or ethanol, and/or water may be introduced to the reaction zone with the carboxylic acid ester and/or alkyl ether feedstock to coproduce carboxylic acid, provided that substantially anhydrous conditions are maintained in the reaction zone. Thus, for example, a controlled amount of methanol and/or water may be introduced to the reaction zone with methyl acetate to coproduce acetic acid with acetic anhydride, provided that substantially anhydrous conditions are maintained in the reaction zone.

Any soluble rhodium containing catalyst useful in the carbonylation of esters or ethers may be used herein. The source of rhodium may be, for example, a simple inorganic salt such as rhodium chloride, bromide, iodide, or nitrate; a carbonyl or organometallic complex of rhodium, or a coordination complex. Finely divided rhodium metal which becomes solubilised in the reaction medium may also be used.

The iodide promoter used in conjunction with the catalyst may be added as elemental iodine, hydrogen iodide, an iodide salt, for example sodium iodide, or an organic source of iodide such as an alkyl or aryl iodide. A preferred source of the iodide component is methyl iodide. It is possible to supply part of the iodide with the rhodium by using, for example, a compound such as rhodium triiodide. The concentration of iodide is such as to produce a rhodium to iodide molar ratio of at least 1:4 preferably between 1:10 and 1:1000.

The co-promoter is present in amounts such that the molar ratio of co-promoter to rhodium catalyst is at least 0.5:1 and preferably in the range 0.5:1 to 10⁵:1. The co-promoters of the present invention may be prepared separately before being introduced to the reaction zone or they may be prepared *in situ* by, for example, a corresponding imidazole being quaternised by a source of alkyl iodide *in situ*. The imidazole itself, may also be prepared *in situ* by alkylation of a less substituted imidazole by a source of alkyl iodide such as methyl iodide.

The carbonylation reaction as described herein is carried out in the liquid phase comprising a solution of the catalyst system. The concentration of the soluble rhodium component will in general be such as to constitute between 10 ppm and 20000 ppm preferably between 10 ppm and 10000 ppm and most preferably between 10 ppm and 3000 ppm of the reaction mixture.

The process is carried out under superatmospheric pressure and at elevated temperature. Although the

optimum conditions will depend on the particular feedstock and catalyst system used, the reaction is generally carried out at a pressure of greater than 10 bars, preferably 10 to 100 bars and at a temperature in the range of 100 to 250 °C. For the preferred feedstocks mentioned herein, the optimum temperature and pressure range will vary somewhat. However, the ranges of such optimum temperatures and pressure for a given feedstock will be familiar to those skilled in the art of carbonylation.

It is preferable that the carbon monoxide used in this invention is as pure as possible. However, a certain amount of diluent gases such as nitrogen or gases which are often co-produced with carbon monoxide, such as hydrogen, may be present. If hydrogen is present it should be at a level consistent with the desired level of by-products which may be produced therefrom. Preferably, hydrogen is present in the reaction zone, at a partial pressure suitably 0.01 to 10 bara, preferably 0.1 to 3 bara.

A suitable continuous process for the present invention is described in our European patent application EP 0087870A, which describes a process for the production of acetic anhydride with or without the net co-production of acetic acid from methanol and carbon monoxide in a series of esterification, carbonylation and separation steps comprising (1) reacting methanol with recycle acetic acid in an esterification step to form an esterification product containing predominantly methyl acetate, water and optionally unreacted methanol; (2) removing part of the water from the esterification product; (3) reacting the esterification product still containing water with carbon monoxide in a carbonylation step in the presence as catalyst of free or combined metallic carbonylation catalyst and as promoter of free or combined halogen to form a carbonylation product containing acetic acid and acetic anhydride; (4) separating the carbonylation product by fractional distillation into a low boiling fraction containing carbonylation feed and volatile carbonylation promoter components, acetic acid and acetic anhydride fractions, and a higher boiling fraction containing carbonylation catalyst components; (5) recycling the low boiling fraction containing carbonylation feed and carbonylation promoter components and the higher boiling fraction containing carbonylation catalyst components to the carbonylation step; and (6) recycling at least part of the acetic acid fraction to the esterification step.

The solubilising and stabilising influence of the co-promoters of the present invention will now be illustrated by way of the following examples.

Preparation of Rhodium Catalyst Stock Solution

A mixture of rhodium triiodide (6.28g, 13.00 mmol), water (28.0g), HI (4.0g of a 57% aqueous solution) and glacial acetic acid (134.0g) was introduced into a 300ml Hastelloy B2 autoclave. The autoclave was sealed and charged to 30 barg with carbon monoxide and heated to 180 °C and maintained at this temperature for 48 hours. At the end of this period the autoclave was cooled and vented. The solution was centrifuged and analysed for rhodium concentration by acid digestion followed by atomic absorption spectroscopy. Typically the catalyst stock solution contained between 2000 - 3000 ppm rhodium. The stock solution was filtered before use.

Preparation of the Quaternised Imidazoles

The quaternised imidazoles according to and not according to the present invention were prepared by treatment of a respective imidazole in tetrahydrofuran with 3 to 4 equivalents of methyl iodide followed by reflux for twelve hours. In some cases the imidazole was alkylated as well as quaternised by the methyl iodide. The quaternised imidazoles and corresponding imidazoles are summarised below. The products isolated from these reactions were further treated with methyl iodide in an acetic acid, acetic anhydride, methyl acetate mixture at 180 °C in a Fischer-Porter tube in the first stage of the solubility/stability test to ensure complete quaternisation of the imidazole.

Examples According to Present Invention	
Quaternised Imidazole	Imidazole
1,3,4-trimethylimidazolium iodide	4-methyl imidazole
1,2,3,4,5 - pentamethylimidazolium iodide	1,2,4,5-tetramethyl imidazole

Comparative Experiments	
Quaternised Imidazole	Imidazole
1,3-dimethylimidazolium iodide	1-methyl imidazole
1,2,3-trimethylimidazolium iodide	1,2-dimethyl imidazole

The imidazoles were supplied by commercial sources.

Solubility and Stability Measurements

Examples According to the Present Invention

Example 1

3.62g of 1,3,4-trimethylimidazolium iodide prepared as described above was added to a solution of acetic anhydride (3.33g), methyl acetate (2.38g), methyl iodide (2.85g) and acetic acid (5.11g). The mixture was then heated in a Fischer-Porter tube for 12 hours at 180 °C under 1 bara nitrogen. At the end of this period the solution was cooled to room temperature and 2.95g of the catalyst stock solution added. The solution was stirred for one hour at room temperature and then sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the solubility of the rhodium catalyst in the presence of the co-promoter.

The remaining solution was heated to 180 °C under 1 bara nitrogen for 22 hours. At the end of this period the solution was cooled and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the stability of the rhodium catalyst in the presence of the co-promoter. The results are shown in Table 1.

Example 2

3.59g of 1,2,3,4,5-pentamethylimidazolium iodide prepared as described above was added to a solution of acetic anhydride (3.31g), methyl acetate (2.38g), methyl iodide (2.67g) and acetic acid (5.12g). The mixture was then heated in a Fischer-Porter tube for 12 hours at 180 °C under 1 bara nitrogen. At the end of this period the solution was cooled to room temperature and 3.00g of the catalyst stock solution added. The solution was stirred for one hour at room temperature and then sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the rhodium solubility in the presence of the co-promoter.

The remaining solution was heated to 180 °C under 1 bara nitrogen for 22 hours. At the end of this period the solution was cooled and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the stability of the rhodium catalyst in the presence of the co-promoter.

The results are shown in Table 1.

Comparative Experiments

Comparative Experiment A

3.61g of 1,2,3-trimethylimidazolium iodide prepared as described above was added to a solution of acetic anhydride (3.31g), methyl acetate (2.38g), methyl iodide (2.86g) and acetic acid (5.11g). The mixture was then heated in a Fischer-Porter tube for 12 hours at 180 °C under 1 bara nitrogen. At the end of this period the solution was cooled to room temperature and 3.00g of the catalyst stock solution added. The solution was stirred for one hour at room temperature and then sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the solubility of the rhodium catalyst in the presence of the co-promoter.

The remaining solution was heated to 180 °C under 1 bara nitrogen for 22 hours. At the end of this period the solution was cooled and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the

stability of the rhodium catalyst in the presence of the co-promoter. The results are shown in Table 1.

Comparative Experiment B

3.65g of 1,3-dimethylimidazolium iodide prepared as described above was added to a solution of acetic anhydride (3.30g), methyl acetate (2.40g), methyl iodide (2.89g) and acetic acid (5.13g). The mixture was then heated in a Fischer-Porter tube for 12 hours at 180°C under 1 bara nitrogen. At the end of this period the solution was cooled to room temperature and 2.89g of the catalyst stock solution added. The solution was stirred for one hour at room temperature and then sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the solubility of the rhodium catalyst in the presence of the co-promoter.

The remaining solution was heated to 180°C under 1 bara nitrogen for 22 hours. At the end of this period the solution was cooled and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the stability of the rhodium catalyst in the presence of the co-promoter. The results are shown in Table 1.

TABLE 1

	Rhodium Solubility (ppm)	Rhodium Stability (ppm)
Experiment 1	317	324
Experiment 2	298	308
Comparative Experiment A	40	42
Comparative Experiment B	36	70

Note: The results in Table 1 have been corrected for small unavoidable losses of volatile components during the experiments.

Examples 4 and 5 and Comparative Experiments C & D

Further experiments were performed using increased amounts of acetic anhydride.

Preparation of Quaternised Imidazoles

Quaternised imidazoles were prepared by treating the respective free base in dichloromethane with 3-4 equivalents of methyl iodide followed by heating to reflux for three hours. The product was isolated by removal of the solvent in vacuo.

Comparative Experiment C

1,3-dimethylimidazolium iodide (2.789g) prepared as described above was added to a solution of acetic anhydride (4.205g), acetic acid (11.511g), methyl iodide (3.111g) and methyl acetate (3.001g). The mixture was then heated in a Fischer-Porter vessel for 12 hours at 180°C under 1 bara nitrogen. At the end of this period the solution was allowed to cool to room temperature and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.0305g) added. The solution was stirred for one hour at room temperature and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the solubility of the rhodium catalyst in the presence of the co-promoter.

The remaining solution was heated to 180 °C under 1 bara of nitrogen for 12 hours. At the end of this period the solution was cooled and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the stability of the rhodium catalyst in the presence of co-promoter. The results are shown in Table 2.

Example 4

1,3,4-trimethylimidazolium iodide (2.368g) prepared as described above was added to a solution of acetic anhydride (4.223g), acetic acid (10.629g), methyl iodide (3.223g) and methyl acetate (3.210g). The mixture was then heated in a Fischer-Porter vessel for 12 hours at 180 °C under 1 bara nitrogen. At the end of this period the solution was allowed to cool to room temperature and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.0298g) was added. The solution was stirred for one hour at room temperature and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the solubility of the rhodium catalyst in the presence of the co-promoter.

The remaining solution was heated to 180 °C under 1 bara of nitrogen for 12 hours. At the end of this period the solution was cooled and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the stability of the rhodium catalyst in the presence of co-promoter. The results are shown in Table 2.

Example 5

1,2,3,4,5-pentamethylimidazolium iodide (2.444g) prepared as described above was added to a solution of acetic anhydride (4.215g), acetic acid (10.991g), methyl iodide (3.330g) and methyl acetate (3.006g). The mixture was then heated in a Fischer-Porter vessel for 12 hours at 180 °C under 1 bara nitrogen. At the end of this period the solution was allowed to cool to room temperature and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.0337g) was added. The solution was stirred for one hour at room temperature and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the solubility of the rhodium catalyst in the presence of the co-promoter.

The remaining solution was heated to 180 °C under 1 bara of nitrogen for 12 hours. At the end of this period the solution was cooled and sampled. The sample solution was centrifuged and the solution analysed for rhodium by acid digestion followed by atomic absorption spectroscopy to provide a measure of the stability of the rhodium catalyst in the presence of co-promoter. The results are shown in Table 2.

TABLE 2

	Rhodium Solubility (ppm)	Rhodium Stability (ppm)
Comparative Experiment D	35	66
Example 4	235	877
Example 5	335	813

Notes: (1) The results have been corrected to allow for small unavoidable loss of volatile components during the experiment.

(2) The stability concentrations are higher than the solubility concentrations due to increased dissolution on heating.

The results in Table 2 show that under adverse conditions the co-promoters according to the present invention support a higher concentration of rhodium in solution than other co-promoters.

Carbonylation Reaction Experiments

Preparation of Quaternised Imidazole - Experiment 6

1,2,4,5-tetramethylimidazole was treated with 3 to 4 molar equivalents of methyl iodide in dichloromethane solvent and refluxed for three hours. The solvent was then removed by vacuum to yield 1,2,3,4,5-pentamethylimidazolium iodide which was used in the subsequent carbonylation reaction.

Carbonylation Reaction in Presence of 1,2,3,4,5-Pentamethylimidazolium Iodide - Experiment 7

1,2,3,4,5-pentamethylimidazolium iodide (9.02g) prepared as above; acetic anhydride (5.21g); methyl acetate (6.81g); methyl iodide (7.96g); acetic acid (21.01g) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.072g) (equivalent to 761 ppm rhodium in the reactor contents) was charged to a 100 ml Hastalloy B2 autoclave. The autoclave was sealed and pressurised to 4 bar gauge with carbon monoxide and heated to 180°C. When a steady temperature had been obtained, the pressure was raised to 41 bar by the addition of further carbon monoxide. The temperature was maintained for 1 hour during which time the uptake of carbon monoxide was measured by pressure fall. At the end of this period the autoclave was cooled and depressurised and the contents analysed by gas chromatography. Yield of acetic anhydride was 3.31g corresponding to a 35.2% conversion of methyl acetate. Reaction rate based upon carbon monoxide uptake was 3.35 mol/kg/h.

Claims

1. A process for the production of a carboxylic acid anhydride comprising reacting in a reaction zone under substantially anhydrous conditions, carbon monoxide with a carboxylic acid ester or an alkyl ether in the presence of a rhodium catalyst, an iodide promoter and a co-promoter characterised in that the co-promoter is selected from the group consisting of:
 - 1,3-dialkyl-4-methylimidazolium iodide;
 - 1,3-dialkyl-4-ethylimidazolium iodide;
 - 1,3-dialkyl-4-n-propylimidazolium iodide;
 - 1,3-dialkyl-4-isopropylimidazolium iodide;
 - 1,3-dialkyl-4-n-butyylimidazolium iodide;
 - 1,3-dialkyl-4-sec-butyylimidazolium iodide;
 - 1,3-dialkyl-4-tert-butyylimidazolium iodide;
 - 1,3-dialkyl-2,4,5-trimethylimidazolium iodide and mixtures thereof where the alkyl groups are independently C_1 to C_{20} alkyl.
2. A process as claimed in claim 1 characterised in that the alkyl groups of the co-promoter are methyl or ethyl.
3. A process as claimed in claim 1 characterised in that the copromoter is selected from the group consisting of:
 - 1,3,4-trimethylimidazolium iodide; and
 - 1,2,3,4,5-pentamethylimidazolium iodide;
4. A process as claimed in any one of the preceeding claims characterised in that the co-promoter is prepared in situ by quaternising a corresponding imidazole with an alkyl iodide.
5. A process as claimed in claim 4 characterised in that the corresponding imidazole is prepared in situ by alkylating a less substituted imidazole by an alkyl iodide.
6. A process as claimed in any one of the preceeding claims characterised in that the process is operated continuously with removal of reaction medium from the reaction zone and with separation from the reaction medium of the carboxylic acid anhydride product prior to recycle of the rhodium catalyst and promoters to the reaction zone.

7. A process as claimed in any one of the preceeding claims characterised in that the carboxylic acid ester or alkyl ether has from 2 to 6 carbon atoms.
8. A process as claimed in claim 7 characterised in that the carboxylic acid ester is methyl acetate or ethyl acetate.
9. A process as claimed in any one of the preceeding claims characterised in that a controlled amount of alkanol and/or water is introduced to the reaction zone with the carboxylic acid ester and/or alkyl ether feedstock to coproduce carboxylic acid.
10. A process as claimed in claim 9 characterised in that a controlled amount of methanol and/or water is introduced to the reaction zone with methyl acetate to coproduce acetic acid with acetic anhydride.
11. A process as claimed in any one of the preceeding claims characterised in that the co-promoter is present in a molar ratio to the rhodium catalyst of from 0.5:1 to 10^5 :1.

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(54) **Process for the production of carboxylic acid anhydrides.**

(57) The solubility and stability of rhodium catalysts in rhodium-catalysed carbonylation of alkyl esters or alkyl ethers under substantially anhydrous conditions to produce carboxylic acid anhydrides is improved by the use of co-promoters selected from the group:
1,3-dialkyl-4-methylimidazolium iodide;
1,3-dialkyl-4-ethylimidazolium iodide;
1,3-dialkyl-4-n-propylimidazolium iodide;
1,3-dialkyl-4-isopropylimidazolium iodide;
1,3-dialkyl-4-n-butylimidazolium iodide
1,3-dialkyl-4-sec-butylimidazolium iodide
1,3-dialkyl-4-tert-butylimidazolium iodide;
1,3-dialkyl-2,4,5-trimethylimidazolium iodide and mixtures thereof where the alkyl groups are independently C₁ to C₂₀ alkyl.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 8628

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	EP-A-0 087 870 (BP CHEMICALS LTD.) * page 7, line 1 - line 30 * * page 8, line 3 - line 6; claims 1-7 * ---	1,2	C07C51/56 C07C53/12
D,Y	EP-A-0 153 834 (BP CHEMICALS LTD.) * page 4, line 17 - page 5, line 5 * * page 5, line 12 - line 21; claims 1-3,5 * ---	1,2	
D,P, A	EP-A-0 391 680 (BP CHEMICALS LTD.) * claims 1,5 * ---	1,2	
A	GB-A-2 106 511 (AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY) * page 2, line 40 - page 3, line 14; claims 1,5 * * page 3 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05 OCTOBER 1992	Examiner KLAG M.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			